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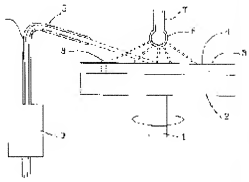
(54) CLEANING METHOD OF OBJECT SURFACE AND CLEANING EQUIPMENT FOR METHOD

(57)Abstract:
PROBLEM TO BE SOLVED: To provide cleaning technique which can eliminate in a short time organic deposit which is especially difficult to be eliminated, without having to resort to physical actions which is likely to damage the function of the surface of a flat material component.
SOLUTION: Base aqueous solution and ozone aqueous solution are supplied simultaneously on the surface of an object whose surface is contaminated by deposit, from a first nozzle 5 and a second nozzle 7, respectively. The surface is made continuous contact a fresh base aqueous solution and an oxygen aqueous solution, and ozone is decomposed on the surface, thereby eliminating the deposit and cleaning the surface of the article.



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CLAIMS

[Claim(s)]
[Claim 1] The defecation approach on the front face of goods of making ozone decomposing on this front face, and removing said affix by a front face supplying an aqueous base and an ozone water solution to the front face of the goods polluted with the affix at coincidence, and said front face continuing in that case, and making it contact a fresh aqueous base and an ozone water solution.
[Claim 2] The defecation approach on the front face of goods of claim 1 which said goods are tabular, is made to move the film of an aqueous base along the front face, and supplies an ozone water solution to coincidence at this solution layer.
[Claim 3] The defecation approach of claims 1 or 2 which added the hydrogen peroxide to the aqueous base.
[Claim 4] The defecation approach of claims 2 or 3 that migration of the aqueous base along the front face of tabular goods is made by supply by rotation of these tabular goods and the nozzle of this water solution.
[Claim 5] The defecation approach of any 1 term of claims 1-4 that the base contained in an aqueous base is chosen from tetramethylammonium hydroxide and hydroxylation trimethyl hydroxyethyl ammonium.
[Claim 6] The defecation equipment of the tabular goods front face on which have in the device which the front face of tabular goods rotates with a perpendicular revolving shaft to the field, the 1st nozzle for aqueous base supply which makes this whole front face produce the flow of the film of an aqueous base, and 1 or two or more 2nd nozzles which supply an ozone water solution on this front face, it is made make ozone decompose all over this front face in, and the heating device for the supply liquid of the 1st nozzle was further attached.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the surface defecation approach except an organic contamination, a particle, etc. adhering to front faces, such as a goods front face especially tabular goods, for example, a semi-conductor silicon wafer, and a glass substrate for liquid crystal, and the equipment for it.
[0002]
[Description of the Prior Art] Improvement in the capacity has always been demanded also for the cleaning method which removes the contamination on a wafer as the device, especially VLSI which use this develop the silicon wafer for semi-conductors. It is of use enough to apply the penetrant remover by which these were developed for the silicon wafer, although improvement in washing capacity is needed with the advancement, other substrates, for example, glass substrate for liquid crystal, for electron devices. Cleaning washing also with more precise thing tabular in electronic parts or a precision machine vessel part article or its ingredient etc. is demanded. The equipment for these and development of an approach are also regarded as influencing from the semi-conductor field in many cases.
[0003] Therefore, the improvement in washing technical of a silicon wafer is important. Although many development has been made in this field, there is still no method which exceeds wet washing about particle removal. When a silicon wafer touches a penetrant remover, a wafer side is charged in negative, but the F-potential of the particle in liquid has many which become negative, when liquid is alkalinity. the APM penetrant remover which consists of aqueous ammonia, a hydrogen peroxide, and water -- (-- a standard presentation -- 1**: -- 1**: -- by 5 **, since the rebounding effectiveness according [an etching operation and a foaming operation] to this static electricity joins Arisa and others, 70-80-degree C processing) is usually widely used for the purpose of particle removal from the former. Although amelioration is performed by the presentation ratio, the device of a cleaning tank, etc., the soak cleaning by APM has been the mainstream of wafer washing for a long time, and has not changed current. The soak cleaning by the choline-hydrogen peroxide by the same mechanism may be used.
[0004] Removal of the organic substance by the wet process is widely used until SPM washing which performs 120-140-degree C processing with the mixed liquor of a sulfuric acid and a hydrogen peroxide is the most powerful and results [from the former] in current. It is removal of the organic substance in a semi-conductor production process, and the important thing with many [and] opportunities is removal of the photoresist which finished the purpose most. Usually, although this resist carried out ashing and is removed with the oxygen plasma, if a resist is completely exfoliated in this case, it will fix to the field after the particle of the ash content containing a metal impurity exfoliating, and that perfect removal will become difficult. Then, it leaves whether it is small in the photoresist film, and, generally it has become a conventional method about ashing a stop and to carry out this SPM processing with a batch method after that for 10 to 15 minutes, and to remove the residual organic substance.
[0005] Since SPM processing uses the same processing liquid from an economic reason many times, the hydrogen peroxide is gradually diluted with the water disassembled and produced. Generally as a photoresist for VLSIs, POJIREJISUTO of a novolak mold is used, and if SPM liquid thins, it will be hard coming to remove HMDS, although the thin layer of the hexamethyldisilazane (HMDS) for improving adhesion with a silicon oxidization film surface in this case is prepared in the resist-oxide-film interface quickly. When the HMDS film remains, abnormalities may be produced at a next process. It is effective to perform APM processing 10 minutes or more, completely removing the HMDS film. Since APM is the alkaline processing which the oxidizing power of a hydrogen peroxide joined, the operation except the

organic substance is also excellent. Therefore, such APM processing is made to follow SPM processing generally in many cases.

0006]

Problem(s) to be Solved by the Invention] Since the concentration of a sulfuric acid is hot high and processing, exhaust air processing requires costs and, moreover, SPM has a problem in a waste fluid processing list in respect of environmental pollution. Moreover, special consideration is required also in respect of the safety of the actuation [itself]. Then, the approach the water containing ozone 20 ppm or more removes a photoresist has appeared. 40 degrees C or less also of processing temperature are sufficient, and also about environmental pollution, since a cure is comparatively easy, many troubles of SPM are solved. That is because ozone shows the strong oxidation to the organic substance. However, according to the experiment which the artificer conducted, in the ozone water solution, it turned out that the HMDS film s hardly unremovable.

0007] On the other hand, the trend of diameter[of silicon wafer macrostomia]-izing is asking for utilization of the sheet method which supplies a penetrant remover, changing to the soak cleaning of the conventional batch method, and carrying out the spin of the wafer. In this case, it is required for the time amount of sheet washing to finish in 2 minutes that it is desirable and 1 minute long from the demand on productivity. Therefore, the approach which detergency accelerates far is more nearly required than the case of the conventional soak cleaning. This invention is going to offer the sheet processing which can remove the HMDS film with the most difficult removal within 1 minute on the organic substance, especially the silicon front face on a silicon wafer.

0008] If the nozzle for penetrant removers supplied to spin washing is used as the nozzle which irradiates the supersonic wave of an MHz band according to the announcement of the latest society etc., in the case of for example, an ozone water solution, electrolysis ion water, etc., depending on the presentation of a penetrant remover, a lot of OH radicals will occur in a wafer side, and removal of the organic substance or a particle will improve remarkably. However, strong MHz ultrasonic cleaning is accompanied by the danger of giving a damage to a detailed pattern, on the wafer in a device production process.

0009] this invention aim at offer the defecate method and the defecation equipment of the goods with which the cleaning effect which be especially excellent to adhesion of the difficult organic substance of removal be acquire , without use the special physical operation with a possibility may give a damage to the front face of goods which make the start components and an ingredient tabular [with a precise and delicate function] , i.e. , MHz ultrasonic irradiation , high pressure jet injection , etc.

[0010]

[Means for Solving the Problem] In order to attain the above-mentioned purpose, by a front face supplying an aqueous base and an ozone water solution to the front face of the goods polluted with the affix at coincidence, and said front face continuing in that case, and making it contact a fresh aqueous base and an ozone water solution, this invention makes ozone decompose on this front face, and offers the defecation approach on the front face of goods of removing said affix. In order for said front face to continue and to make it contact a fresh aqueous base and an ozone water solution, goods may be rotated and/or the supply approach of each water solution may be changed.

[0011] As one gestalt of this defecation approach, goods are tabular, and along that front face, this invention moves the film of an aqueous base, injects an ozone water solution to coincidence at this solution layer, and offers the approach of removing the affix of this front face, by making ozone decompose on this front face.

[0012] In order to attain this purpose more effectively furthermore, in case the defecation approach of this invention carries out the above-mentioned processing, it is desirable to carry out by adding a hydrogen peroxide into an aqueous base.

[0013] Moreover, since this invention is suitable for sheet processing, it performs migration of the aqueous base along the front face of tabular goods by supply by rotation of this plate and the nozzle of this water solution, and offers the defecation approach on the tabular front face of goods into which inject the above-mentioned ozone water solution on this front face, and ozone is made to decompose.

[0014] In addition, the device which uses as the equipment which can enforce the defecation approach of this invention, and the front face of tabular goods rotates with a perpendicular revolving shaft to the field, The 1st nozzle for aqueous base supply which makes this whole front face produce the flow of the film of an aqueous base, Have 1 or two or more 2nd nozzles which inject an ozone water solution, it is made to make ozone decompose all over this front face on this front face, and the defecation equipment of the tabular goods front face on which the heating device for the supply liquid

of the 1st nozzle was further attached is offcred.
[0015]
[Embodiment of the Invention] Although the following explanation is given especially about tabular ingredient components as a typical example when goods are tabular, it is not limited to this.
[0016] An alkaline penetrant remover has remarkable removal capacity depending on the class of organic substance according to the saponification operation. This invention tends to make the capacity have a logical jump according to generating of the radical accompanying decomposition of ozone. As mentioned above, in washing of a silicon wafer, basc-hydrogen-peroxide washing was the most powerful thing that served both as organic substance removal and the particle removal effectiveness. This invention tends to strengthen a cleaning effect extraordinarily also about this using generating of the radical accompanying decomposition of ozone. Therefore, the gestalt of the optimal operation is shown as what made the generating conditions of a radical the optimal.
[0017] When the water solution of a base is mixed with the water solution of ozone, it is OH of an aqueous base. - Ozone water is disassembled so quickly that solution temperature is so high that ion concentration is high again. For example, when pH is 13, ozone disappears substantially in several seconds also at a room temperature. The mechanism of the reaction of this ozone of decomposition has been considered to be radical reaction for many years. J. According to Weiss (Trans.FaradaySoc.Vol.31,668 (1935)), it is HO2 first as follows. A radical is made and it is O3 by chain reaction. It decomposes. OH radical to generate also participates in this chain.
[0018]
O3+OH-->O2-+ -HO2 -- Chain initiation O3+ -HO2 ->2O2+ -OH O3+ -OH->O2+ -HO2 -- Reaction chain 2 -HO2 ->O3+H2 O -HO2+ -OH->O2+H2 O -- A chain termination reaction is exothermic reaction and tends to occur on a substrate front face. That is because a substrate absorbs the high energy which the system of reaction emits. Therefore, it is OH in a place with the ozone molecule of an ozone water solution near a substrate side. If ozone water is injected so that it may meet with ion, a radical occurs, it is easy to decompose ozone, and it is not necessary to perform high-pressure injection for that purpose especially. - HO2 Since a radical and OH radical have the very strong operation which disassembles the organic substance, by the base independent, the organic substance which is hard to disassemble also serves as effectiveness of the heated aqueous base removable easily conjointly.
[0019] A chain initiation type shows that the yield of a radical also increases, so that the concentration of a base is high. However, if concentration of a base is only made high, a harmful etching operation will be produced to a silicon side. It is also one of the reasons this operation will be controlled if the hydrogen peroxide is added, and base-hydrogen-peroxide washing is used in the semi-conductor field. However, using the aqueous base which added the hydrogen peroxide by this invention expects still more positive effectiveness about organic substance removal.
[0020] It is also known for many years that a hydrogen peroxide will act as a catalyst which accelerates decomposition of ozone. It is related with the ozonolysis of the base by the above-mentioned chain reaction, and is H2 O2. Coexistence is HO2 to OH list. Generating of a radical is made to increase and this decomposition is accelerated. The chain reaction mechanism considered is -OH+H 2O2. ->H2 O+ -HO2 and HO2+H2 O2 ->O2+H2 O+ It is -OH. Decomposition of the organic affix on a substrate side is further accelerated by the radical which these-increased, and it is removed effectively.
[0021] The powerful organic substance removal operation by such radical has effectiveness in particle removal, and is added to the particle removal operation based on the F-potential known well. The particle on the substrate side exposed to the clean room has usually fixed to the substrate side by liquid bridge formation of organic contamination film, such as DOP. It is difficult for a slight etching operation of base-hydrogen-peroxide processing to carry out lift off of this fixing particle in short-time sheet spin washing. However, according to the radical operation of this invention, the liquid bridge formation organic film can be removed and this fixing particle may be made to secede from it.
[0022] It is simply more desirable to use a strong base from the ammonia of a weak base as an object of this invention, if a radical yield is related to OH ion concentration. However, since organic decontamination capacity is far stronger than the below-mentioned thing at the APM itself, it may use according to the purpose and the presentation may be proportionate to APM. Although disliked in the semi-conductor field, the inorganic strong base containing a metallic element like NaOH or KOH is useful when the washed body is a metal. Operating concentration applies to the following organic things correspondingly.
[0023] As a strong base which does not contain the metallic element for the semi-conductor field, the tetramethylammonium hydroxide (TMAH) and hydroxylation trimethyl hydroxyethyl ammonium (cholinc) of an organic strong base are desirable. the hydroxycthyl radical which it has to the latter -- formula-(CH2CH2O) mH -- [-- however,

as for m, it is desirable that the strong bases permuted by 2 or 3] are contained. These can fully raise a cleaning effect in an about 0.1-0.01-mol thin water solution. Depending on the candidate for washing, even about 10 ppm very thin liquid is effective. It is desirable to use it with a hydrogen peroxide in the semi-conductor field, and the concentration has 50 times to effective isoconcentration extent of an organic strong base at weight %. About 5 times is desirable from 20 times. Since it is rare to pollute an environment with no odor and the formed mol concentration which needs decomposition with an abandonment cover coat article is slight, abandonment processing is easy for most these. Therefore, it is most suitable when carrying out this invention.

[0024] The thing high as much as possible of the ozone level of the ozone water solution to inject is desirable. The saturated concentration of ozone is proportional to the ozone level in the gas to introduce. Since the high grade ozone generator of a discharge method is usually the ozone level of 200 mg/l extent, when saturating this in the water of a room temperature, it becomes 30 ppm order. In the case of this invention, temporary effectiveness is accepted also in an about 10 ppm ozone water solution. In this invention, MHz ultrasonic irradiation or high-pressure jet injection with a possibility of giving a damage to the condition and function in a front face on the occasion of injection of ozone are not needed to a substrate side. However, since these physical operations are very effective in radical generating, when there is no fear of such damage generating, in this invention, concomitant use with these physical operations may be desirable.

[0025] When requiring a powerful cleaning effect like HMDS film removal, since it is above, it is desirable to add a hydrogen peroxide. This is because the particle removal effectiveness is strengthened with generating a radical strongly on a substrate front face by the organic substance list of base-hydrogen-peroxide washing used from the former. Generally warming accelerates radical generating. Therefore, it is desirable that the temperature of an aqueous base is 40-80 degrees C in processing of this invention in respect of effectiveness, and further 50-70 degrees C is desirable. If temperature is high, liquid will foam and supply for a desirable nozzle cannot be performed. Then, the 1st nozzle is made into 2 reams, in one piece, the hydrogen-peroxide-solution solution which heated the heated aqueous base by one piece is injected, and addition may be performed on a plate front face.

[0026] When using an organic strong base, it is TMAH or 0.05 - 0.2% of the weight of a choline, and H2 O2. If 0.5 - 5% of the weight of a water solution is used, even if processing liquid itself has the weak capacity to compare with APM and to remove the organic substance and it applies it to the mere immersion processing it is [processing] 70 degrees C, it can hardly remove the HMDS film. However, if this invention is carried out with the liquid of the same presentation, it will become removable [the HMDS film] within 1 minute. This processing liquid is OH. - It is because ion concentration is high and the washing acceleration by the radical is performed powerfully.

[0027] For moving the thin solution layer of an aqueous base in the substrate side for electron devices, two methods are practical. One rotates a substrate with a perpendicular revolving shaft to a substrate side, and it uses the device which emits this liquid from an oblique position by the nozzle to a substrate side. When a revolving shaft takes the lead in a substrate, it is the same device as spin washing. Rotation is good at 700 - 1500rpm. It is also possible to arrange two or more substrates around a revolving shaft. In the case of the former, the sense of a nozzle is a center of a substrate, in the case of the latter, a nozzle prepares for every substrate, and emission is performed from a revolving-shaft side. To the substrate of a square shape, other one is effective, it arranges a substrate side perpendicularly, and makes it flow down this liquid from the upper part.

[0028] It is HO2 which generates very important one in this invention. When the life of a radical or OH radical injects an ozone water solution to a substrate side very short (below a ms), in the flow of this liquid on a substrate side, only the area near the attainment location on a field is that an operation of a radical does not reach. For example, when liquid membrane is made to the silicon side which emitted 0.1% of the weight of rare choline water from the nozzle of an oblique position with the spin washing station of 1000rpm, and applied HMDS and a 10 ppm ozone water solution is perpendicularly introduced into an attempt by part for 300ml/in the core of a wafer, the field where HMDS is removed is only in a circle with a radius [of the center of a wafer] of about 3cm. Therefore, it is necessary to open two or more holes at the tip of the 2nd nozzle on the occasion of practical use, and it is necessary to adjust the location, and magnitude and a configuration of a hole so that radical reaction may progress all over a wafer by the group of an injection ozone water solution. In order to advance radical reaction all over a wafer, if two or more 2nd nozzles for ozone water-solution supply are prepared, it will become easy to spread widely a radical reaction field.

[0029] As an ingredient of a part with which the liquid in equipment flows, fluororesins (PTFE, PFA, etc.) list quartz glass is required. However, since alkaline liquid decomposes immediately, usual plastics is enough as ozone about a case, a wastewater instrument, etc. of equipment. Although an example explains this invention below, this invention is not

limited at all in these examplcs.
[0030]
[Example] It was used for the expcriment in each example, and bubbling of what passed about 1l. /of oxygen which contains 1% of nitrogen in the ozone generator of a small discharge mcthod a minute, and was made into ozone level about 200 mg/l was carried out to the pure water which is I0-15 degrees C in the quartz-glass container in which feeding with pressurization air is possible, and the **** ozone water solution created it. Thc ozone level stopped bubbling in the phase which amounted to 10-30 ppm, and fed for the 2nd nozzle by the predetermined rate of flow.
[0031] The quantitative evaluation of the residual organic substancc after washing cut down the 2cmx2cm chip from the wafer immediately after finishing washing and desiccation, and performed it in quest of thc surface residual carbon content by the charged particle activation analysis using the 12C(d, n)13N nuclear reaction shown in Anal.Chem.Vol71.p3551 (1999). At the load map which Semiconductor Industry Association announced in 1997, the amount of organic carbon is set to I.8x1013 atom / cm2 by DRAM256G bit in 2009. Then, when the analysis result was below this value, it decided to fully have made organic decontamination.
[0032] All the examples were carried out in the clean room of the class 10 by which the organic pollution control from the environment which equipped chemical filters, such as activated carbon, was made certainly. Even if this environment exposes the silicon chip immediately after thermal oxidation for 24 hours, the amount of contamination organic carbon contamination in the meantime is managed by the above-mentioned charged particle activation analysis by two or less cm [2x1013 atom / cm] specification.
[0033] It is a tcsting devicc for this invention having converted the sheet spin phosphorus sir dryer which can rotate to 4000rpm currently used from the [example 1] former, and having added the nozzle which supplies liquid to the wafer indicated the vertical cross section to be to drawing 1 notionally. The silicon wafer 4 of the washed body is held with four support columns 3 made from PTFE on the disk 2 made from PTFE which rotates with a revolving shaft I.
[0034] The 2nd nozzle 7 made from quartz glass for ozone watcr solutions which carries out termination in the spherical section 6 which prepared the 1st nozzle 5 (below - of a dotted line that shows the injection direction of liquid is the same) made from PTFE which can inject the water solution of a base towards the center of a wafer mostly from an oblique position, and the pore for acquiring two or more thin jets was equipped. The location and magnitude of pore were created so that the injection section might draw the concentric circle of ****** mostly. The calorifier 9 which used the quartz-glass coil on the way is inserted in the introductory tubing (product made from PFA) 8 to the 1st nozzle. Although not shown in drawing, there is an established nozzle for ultrapure water rinses independently. The part except the calorifier section of drawing is stored in thc container made from polyethylene (not shown) which can seal and has an exhaust port in a bottom.
[0035] Intentionally contamination of the sample with which washing was presented was bascd on HMDS spreading. What performed processing for 1 minute at 100 degrees C including ****** after spreading was used. The water solution of a base used APM. however, a presentation -- aqueous ammonia: -- hydrogen-peroxide: -- water =1**: -- 1**: -- they are 12 **. In APM, foaming becomes intense, so that temperature is high, whcn it heats. Since there was little foaming even if it heated, when the trade name HIRINPER hydrogen peroxide with which the special chelating agent of a minute amount is added was used, also whenever [stoving temperature] was made into 50 degrees C using this. Setting rotation of a wafer to 1000rpm, APM of the 1st nozzle is a part for 300ml/, and the 2nd nozzle is a part for 300ml/about an ozone water solution with a concentration of 20 ppm, and performed injection for 1 minute to coincidence.
[0036] When the ultrapure watcr rinse for I5 seconds was performed from the rinse nozzle succeeding this processing, rotation was once suspended and the front face was observcd, it turned out that the whole surface has got wet, it has hydrophilic-property-ized, and HMDS can be removed once. Spin desiccation was performed by 4000rpm after this, the 2cmx2cm sample was immediately started by the center section and periphery of a wafer, and charged particle activation analysis of a residual carbon content was performed. A center section is [7x1012 atom / cm2 peripheries] 1.0x1013 atom / cm2, and the analysis result has fully rcmoved the HMDS film by this washing processing.
[0037] The ozone water solution of the 2nd nozzle of [the example 1 of a comparison] was not injected, and also it completely carricd out likc the example I. That is, spin washing for [it is based on APM] 1 minute was performed. When rotation was once suspended after the pure-water rinse, thc front face was quite still hydrophobicity. By the same charged particle activation analysis, in 1014 - 1015 atom / cm2, HMDS remains considerably and a residual carbon content cannot say that there was a cleaning effect.
[0038] Although the operation from which the APM itself removes the organic substance has a strong advantage in the

[example 2] example 1, considcration with it is required for wastewater. [a strong ammonia smell and] [remarkable to an antipollution measurc] Morcover, APM NH3 itself There is also about one mol and a load is large also in rcspect of waste water treatment. Then, organic substance decomposition capacity is choline-H2 O2 in which most smells do not have a base and a remarkable particle clcaning effect morcover has it by about 0.01 mols although it is inferior. It experimented like the example 1. The supply liquid to the 1st nozzlc liquid was madc into 0.1 % of the weight of cholines, and high grade H2 O2 2 % of the wcight. It compared with APM, and since there was little foaming, also whenever [stoving tcmperature] was made into 70 degrees C. Others were completely pcrformed like the examplc 1. The wholc surface became a hydrophilic property just behind the ultrapure water rinse, the residual carbon contcnts of the result of the charged particle activation analysis immediatcly after desiccation are two or less 1x1013 atom / cm, and the HMDS film can fully be removed.

[0039] The ozone water solution of the 2nd nozzle of [the example 2 of a comparison] was not injected, and also it completely carried out like the example 2. The charged-particlc-activation-analysis result immediately after washing / desiccation is set to two or more 1x1015 atom / cm, and most HMDS film cannot be removed.

[0040] The 2nd nozzle of the [example 3] example 1 needs dclicate adjustment about processing of thc nozzle hole of a spherical cdge, and it is difficult for it to make that to which the property was equal. So, in this example, it considered as the method which makes an ozone water solution inject with two or more simple tubed nozzles. A bore prepares the 2nd three nozzles of the abbreviation 1/2 of the 1st nozzle instead of the 2nd nozzle 7 with the equipment of an cxample 1. A bird's-eye view shows the arrangement to drawing 2 . the location of the nozzlc 5 for aqucous bases is removcd above a wafer 4, and the 2nd three nozzle 10, 11, and 12 servcs as an include angle each direction of whose is about 120 degrees -- as -- about [moreover, / of a core and a core to a wafer radius] -- the location list of one third of distance -- about -- it is arranged so that it may inject from an oblique position towards the wafer side top of the location of two thirds of distance. The ozone water solution was made to blow off from each 2nd nozzle by part for 100ml/, and also it carried out completely like the example 2. For the result of the charged particle activation analysis immediately after washing / desiccation, residual carbon is two or less 1x1013 atom / cm, and it turned out that HMDS is removable like a last example.

[0041] The choline of the aqueous base in the [example 4] example 3 was changed to TMAH, and othcrs wcrc completely carried out like the example 3. Namely, as for the aqueous base, 0.1 % of the weight of TMAH(s) and H2 O2 2% of the weight of a presentation were used. For the result of the charged particle activation analysis immediately after washing / desiccation, residual carbon is two or less 1x1013 atom / cm, and it turned out that HMDS is removable like a last example.

[0042] In order to investigate the particle removal capacity of [example 5] this invention, RI tracer method evaluated by activity strength reduction by washing by using radioisotope as a marker was used. Namely, half-life 6 hours Made the carbon particle which carried out the indicator from 99mTc using the technegas cquipment for a medicine diagnosis (Appl.Radiat.Isot.Vol46, p157 (1995)), this particle was made to adhcre to the silicon wafer front face which carried out HMDS spreading, and the intentionally contamination sample which carried out liquid bridge formation with the organic substance, and made removal difficult was made. Most of the size of a carbon particlc is 0.05-0.2 micrometers. It can judge by the shade of an image whether intentionally contamination of a particle was mostly made by homogeneity all over the wafer by exposing this wafer by the imaging plate and performing radio RUMINOGURAFI analysis. In this case, melanism was mostly carried out to homogeneity and the radiation intensity which a particle emits was 6300 PSL/mm2 on the average (radio RUMINOGURAFI unit). A choline-hydrogen pcroxide / ozone water treatment was performcd completely like the example 3 to this sample. When analyzed by exposing a wafer by the imaging plate after washing / desiccation, the image completely became only a background. namely, activity -- an average -- 2 PSL/mm2 it was . Therefore, it turns out that even the particle which fixed by the liquid bridge formation device on the organic substance film by this invention is fully removed.

[0043] In order to evaluate the cleaning effect over the organic substance adhering to the glass plate for [cxample 6] liquid crystal, we decided that the quartz-glass plate which carried out intentionally contamination is made applicable to washing, and carries out a simulation. Technique is the same radioactive tracer as a last cxamplc. The quartz-glass plate prepared thc 20cmx20cmx4mm plate, and set it as the object of intentionally contamination of DOP by which the amount of organic contamination from a clean room ambient atmosphere is made [most]. First, by 14C, DOP which carried out the indicator was compounded and it applied at random [one side of a quartz-glass plate] to 15 places. The condition of intentionally contamination as well as an example 5 is imaged in exposure and its analysis of an imaging plate, and it

checkcd that the deepest fields were 2x1016 atom / cm2 by 14C concentration. Thcn, the washing testing device as showed the concept of equipment to drawing 3 by the vertical cross section washed. The quartz-glass plate 13 was set to the guide frame 14 made from PTFE, and was made into washed ****. This was movcd upwards with 15cm speed for /through between the rotating fluororcsin fiber brushes 15 of the shape of two roll from the lowcr part. From two or more nozzles 16 prepared in the front flesh-side both sides of washed ****, if a TMAH water solution is dropped at the contact surface of a roll and a plate 0.1 80-degree C% of the weight, liquid will flow down along with a washed body plate surface. Supply volume was taken as a part for 300ml/per one side. The 30 ppm ozonc water which pore (nozzle hole) is in the perpendicular scnse every 2cm at the quartz-glass tubing 17 and 18 formed in two steps of upper and lower sides, and is supplied in tubing in space at the front flesh side of washed **** is injected by the front rear face of washed **** from this pore. While this glass tube attaches the device in which 2cm amplitude reciprocates in the die-length direction and the flowing-down liquid of a plate surface spreads all over a plate in this actuation, ozone decomposes and washing is performed. After washing of the whole plate surface finishes, a stop and both the rolls 15 are detached for supply of TMAH liquid, the liquid supply from quartz tubes 17 and 18 is switched to ultrapure water, washcd **** is dropped, and a rinse is performed. After spraying and drying the high-pressure high grade nitrogen after descent, it exposed by the imaging plate. According to the analysis, 14C concentration of the field which was the highest as for concentration was decreasing to 8x1012 atom / cm2 before washing. Therefore, DOP was removable enough, even if there was no addition of a hydrogen peroxide to a base.

[0044] Since a [example 7] aluminum side tends [very] to adsorb the organic substance in an environment, if it fully surrounds with the aluminum plate except the organic substance when transporting the tabular sample which is easy to reccive organic substance contamination to a chemical laboratory for organic substance analysis, it can prevent organic contamination of the sample from a migration environment. Then, washing of an aluminum plate was performed using the equipment of an example 6. Since the front face of the sample before washing was carrying out organic contamination, the waterdrop contact angle was 32 degrees. Everything but the combination of the thin aqueous base containing TMAH10ppm and H2 O2 200ppm and 10 ppm ozone water was processed completely like the example 6. The waterdrop contact angle after washing became 4 degrees or less. Organic contamination is substantially removable.

[0045]

[Effect of the Invention] in all, such as alkali cleaning used for metal finishing including base-hydrogen-peroxide washing of the semi-conductor field etc., this invention boils the capacity of organic substance removal and particle rcmoval markedly especially by the radical produced in an ozonolysis, and can be strengthened. It is H2 O2 especially by meeting of a base and ozone. Although a radical occurs as a catalyst, especially this reaction occurs from it being easy to happen on a solid-state front face on a front face with contamination. And the life of a radical is very short. Then, improvement in the throughput whosc this invention combined by shect processing and liquid injection in ordcr to make this meeting hold efficiently on a tabular components ingredient front face was the essential technical problem of sheet processing was closed if . That is, although the washing time amount which powerful washing takes uses the physical operation with a possibility of giving a damage to the condition and function in a front face and drops off, it will end in about 1 minute. It was used at the usual photolithography process, and although removal sufficient in a short time of the HMDS film which needs the perfect removal after use was not completed in wet washing effective in particle removal from the former, it made even this possible.

[0046] The ozone used on the occasion of operation of this invention has the advantage which it does not take a special cure about the container which stores this equipment, or the utility for wastewater exhaust air since it disappears for a short time completely in alkaline liquid. It is only the base which is finally influenced to an environment about opcration of this invention. In this case, if a choline is used, this base will be the physiology matter important originally, and will be biodegraded easily. Therefore, therc is an advantage which can be completely processed in the usual septic tank.

[0047] as long as an organic strong base is used as a base, there is almost no generating of the harmful gas which pollutes a clean room ambient atmosphere, and the equipment of this invention will come out, if an easy airtight and an exhaust air facility are satisfied, and it can install it in a general clean room environment. That is, a draft facility is not necessarily needed. Therefore, there is an advantage which can wash with in-line one.

[0048]

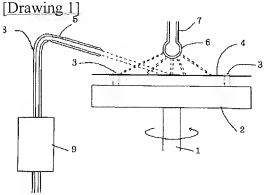
[Translation done.]

* NOTICES *

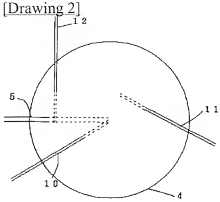
1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DRAWINGS

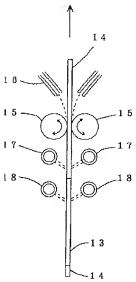
[Drawing 1]



[Drawing 2]



[Drawing 3]



[Translation done.]